

Semiannual Status Report

NASA Research Grant NsG-343, to the
University of Southern California

June 1, 1966

Prepared by R. Simha

R. A. Haldon and Th. Somcynsky

FACILITY FORM 802

~~N 66~~ 84370
(ACCESSION NUMBER)
3
(PAGES)
CR 15349
(NASA CR OR TMX OR AD NUMBER)

(THRU)

None
(CODE)

(CATEGORY)

~~FC~~

1. MULTIPLE TRANSITIONS IN VARIOUS POLYMER SYSTEMS

a) Volume Temperature Measurements

b) Dynamic Mechanical Measurements

a) The instrument for length-temperature measurements down to liquid nitrogen temperatures has been assembled. The dilation of a cylindrical specimen is detected by a linear variable differential transformer (LVDT) and automatically recorded. The observed length-temperature functions are differentiated by the least square technique described in a NASA Technical Report by Zakin and Simha on the polyethylene-polypropylene system.

The system studied to this point is a series of poly-alkyl methacrylates where the alkyl side group is increasing in size. Measurements on poly-ethyl, poly-n-propyl and poly-n-butyl methacrylates indicate two transitions approximately 40°C and 80°C respectively below T_g . Evidence of a further transition exists at about -120°C and of yet another just above liquid nitrogen temperature and beyond the limit of accurate detection with the present coolant. The -120°C transition is similar in location to the polyethylene γ -transition and possibly due to motion of the alkyl chain part of the pendant group. One or both of the transitions immediately below T_g may be related to the β -transition in polymethyl methacrylate. It is possible that these two transitions were not separable by the intersecting straight lines technique conventionally used in volume dilatometry. Further data are being obtained on polymethyl methacrylate, the other isomers of poly-butyl methacrylate, and hydroxy ethyl and hydroxy propyl methacrylates in an attempt to assign the molecular motions associated with these transitions.

Poly-alkyl methacrylates deviate strongly from the $\Delta\alpha \cdot T_g$ free volume product of Simha and Boyer, presumably due to side group motion requiring free volume. If α_g , the expansion coefficient corresponding to the lower of the two transitions immediately below T_g , or $\Delta\alpha = \alpha_l - \alpha_g$ is substituted for $\alpha_l - \alpha_g$, the product assumes a value of 0.11, in accord with values observed for linear polymers.

Measurements of expansion coefficients above T_g have been disappointing with the present set up. We are considering a recording volume dilatometer, incorporating the LVDT.

b) A freely oscillating torsional pendulum of frequency about 1 cps. has been constructed here and is now, in operation down to liquid nitrogen temperatures. It is intended to study the same polymers, in order to obtain comparisons between the two types of information.

2. EQUATION OF STATE PROPERTIES OF POLYMER LIQUIDS

Extensive computations of the equation of state properties predicted by the hole theory for both spherical fluids and polymer liquids were made. We compared two assumptions for the dependence of the cell partition function on the number of vacancies, one based on an average over "solid-like" and "gas-like" free volumes, and the other on a similar average over individual modes of motion or degrees of freedom. To evaluate most rigorously the merits of the theory, we need to test it in a system where the characteristic energy and volume parameters are independently known, such as liquid and gaseous argon. The agreement between experiment and predictions of the hole theory, with an average over modes of motion, is very gratifying. In particular, the critical pressure and temperature are very well predicted.

Due to the lack of independent knowledge of the pair potential parameters for chain liquids, the comparison between theory and experiment can only be made by a superposition procedure. The results of the two alternative assumptions are rather similar, contrary to what is observed in the case of argon. This suggests that any agreement between theory and experiment for polymers reflects in part the shifting procedure used, rather than solely the intrinsic adequacy of the theory. Nevertheless, since a similar treatment was applied to the data in conjunction with the cell theory, we can conclude that the introduction of vacancies into the lattice in an appropriate way results in an improvement over the original cell theory.

3. PUBLICATIONS AND INVITED PAPERS PRESENTED

Principle of Corresponding States and Equation of State of Polymer Liquids and Glasses, V. S. Nanda, R. Simha and Th. Somcynsky, J. Polymer Sci., C12, 277 (1966).

Low Temperature Thermal Expansivities of Polyethylene, Polypropylene, Mixtures of Polyethylene and Polypropylene, and Polystyrene, J. L. Zakin, R. Simha and H. C. Hershey, J. Appl. Polymer Sci., in press.

Some Consequences of the Gibbs-DiMarzio Theory of the Glass Transition,
J. Moacanin and R. Simha, J. Chem. Phys., in press.

Hole Theory for Spherical and Polymer Liquids, Th. Somcynsky and R. Simha,
in preparation.

The Equation of State Properties of Polymer Liquids and Glasses,
presented at the University of Florida.

Equation of State Properties of Amorphous Polymers, invited paper at
Am. Phys. Soc. Meeting, Durham, N. C.

Equation of State Properties of Amorphous Polymers, Lectures on Polymer
Science and Technology, Rensselaer Polytechnic Institute.